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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

03 Sept 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-210**
Rusty Blanski; Brent Viers; Rene Gonzalez; Andre Lee; Shawn Phillips (PRSM), "The Synthesis and Characterization of Lubricants Based on POSS Technology" (viewgraphs)

POSS Nanotechnology Conference
(Huntington Beach, CA, 25-27 September 2002) **(Deadline: 25 Sept 02)**

(Statement A)

The Synthesis and Characterization of Lubricants Based on POSS Technology

27 September 2002

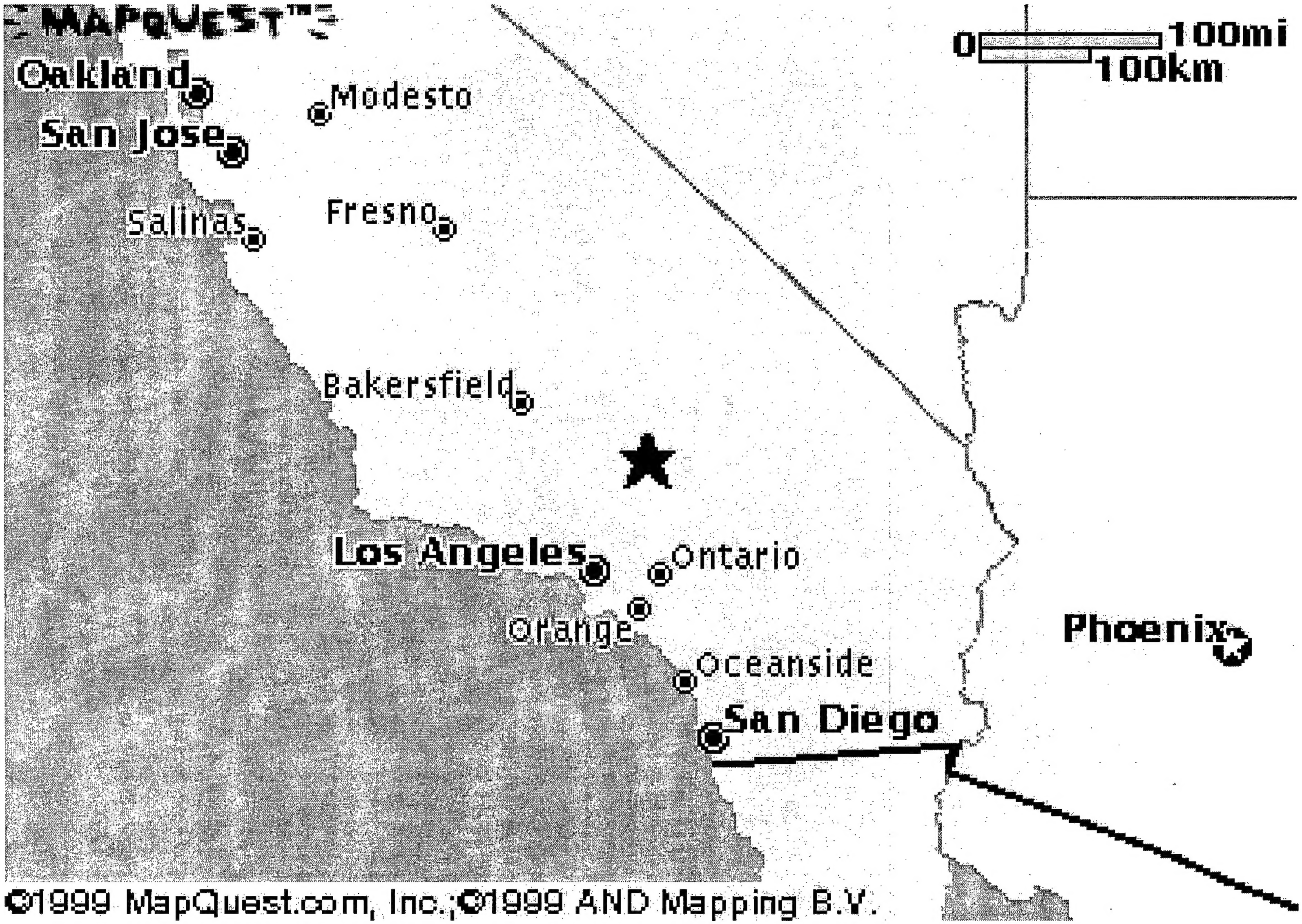
Rusty Blanski, Brent Viers, Rene Gonzalez, Andre Lee, and Shawn H. Phillips

PRSM

Air Force Research Laboratory

Air Force Research Laboratory

Located ~ 100 miles from LA



POSS Lubricants Project

- Goal

- Develop a lubricant that can withstand high temperatures (600 ºF goal in IHPTET Phase III) and flows at -40 ºC (20K centistoke) (High temp gas turbine engines: jets)
- Higher temperature lubes means higher operating temperature which can lead to more power: increase in thrust:weight ratio

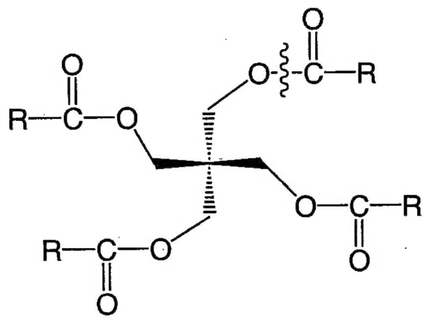
- Objective

- Synthesize a POSS oil with an operating range of -40 ºC to >> 400 ºF (450 ºF minimum)

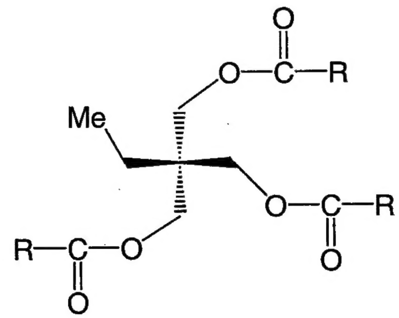
- Technical Hurdles:

- Reaching High temperature operating minimum (450 ºF)
- Current Antioxidants in AF inventory decompose POSS

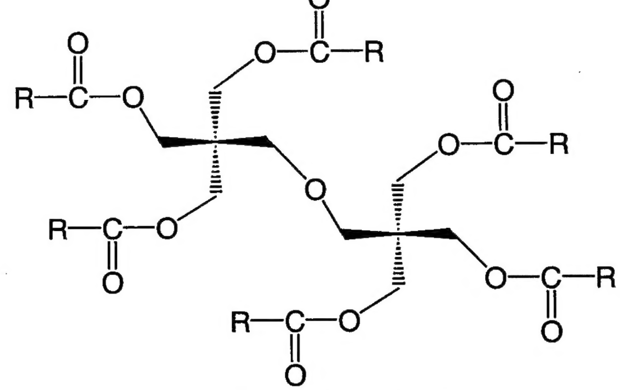
Present AF Lubricants Technology



Pentaerithritol Ester



Trimethyloproane Ester

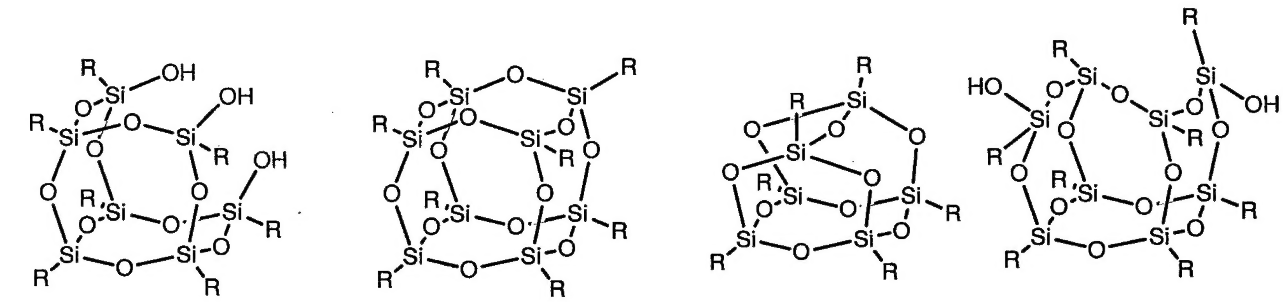


Pentaerithritol Dimer Ester

- The above polyol ester compounds are the main components of some AF turbine lubricants
- Operating range of –40 °C to 200 °C
- In house calculations show that ester C-O linkage breaks at 200 °C
- Aminic antioxidants used

POSS = Polyhedral Oligomeric Silsesquioxane: Pre Hybrid Synthesis

$RSiCl_3 + H_2O \longrightarrow$



R =Cyclohexyl
Cyclopentyl
Cycloheptyl
Vinyl
Methyl

R = Cyclohexyl
Cyclopentyl
Cycloheptyl

R =Cyclohexyl
Cyclopentyl
Vinyl
Methyl

R = Cyclohexyl

R = Cyclohexyl

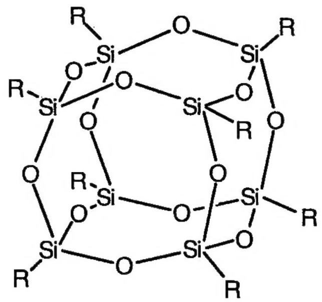
R=Cyclohexyl: Brown and Vogt 1965
Feher, Newman, Walzer 1989
Lichtenhan (AFRL, mid '90's) Optimized Purification

Cyclopentyl: Feher, Budzichowski, Weller, Blanski, Ziller 1990
Lichtenhan (AFRL, 1993) Optimization

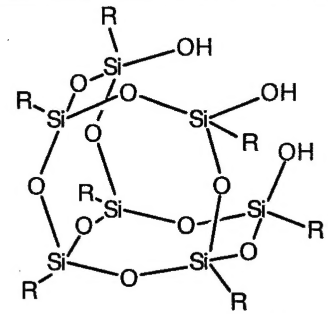
All of these materials are colorless solids at ambient temp

POSS Diversity

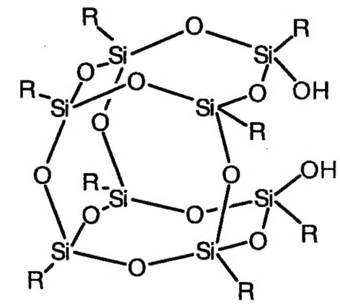
Hybrid Plastics



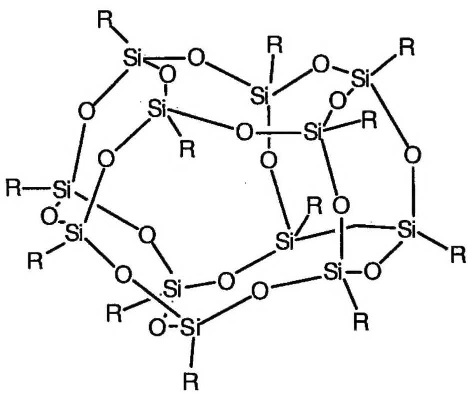
R = Methyl
Isobutyl
Cyclopentyl
Cyclohexyl
Phenyl
Phenethyl
Octadecene



R = Isobutyl
Cyclopentyl
Cyclohexyl
Isooctyl
Ethyl



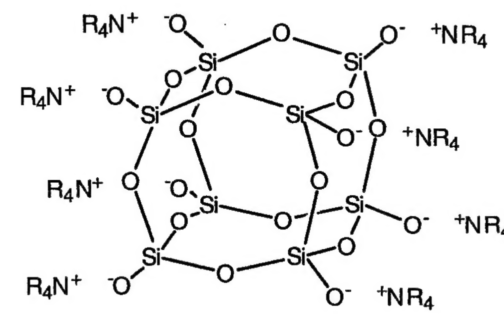
R = Isobutyl
Cyclopentyl
Cyclohexyl
Isooctyl



R = Phenyl
Trifluoromethylpropyl

Cage Mixtures
(T_8, T_{10}, T_{12})

R = Vinyl
Phenethyl
Isooctyl

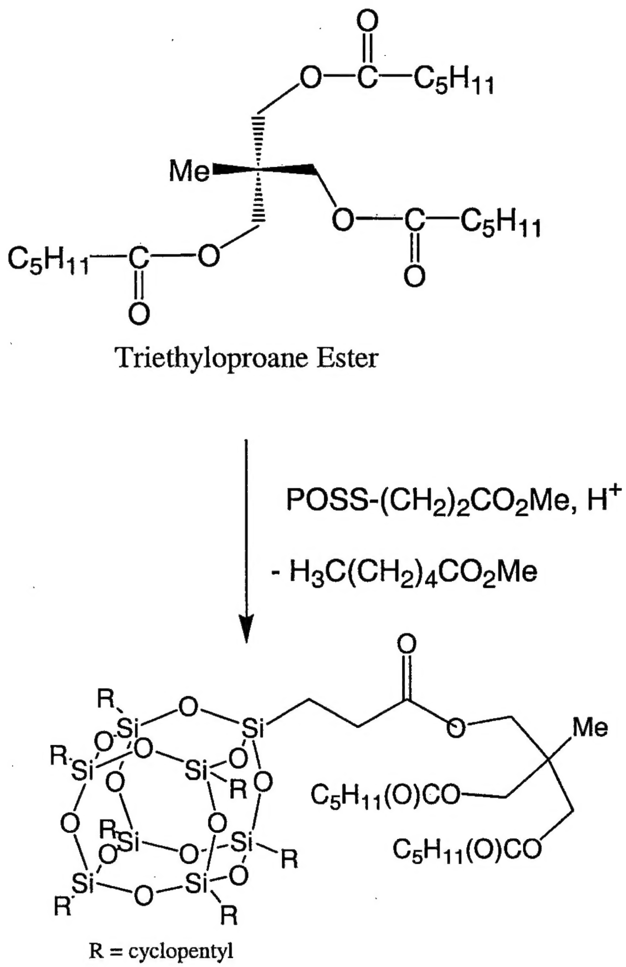


R = Methyl

POSS Esters

- Goal: to synthesize a POSS Ester either as a lubricant additive or as a drop-in replacement
- It is believed that the POSS can act as a heat sink that will slow the ester decomposition so that higher temperatures can be reached (> 400 °F)
- Technical Issues:
- \- Lubricant Additives can be a solid (what all POSS esters are now) where an oil would be preferred
- \- Drop-in replacements need to follow the standard parameters (flows at – 40 °F)

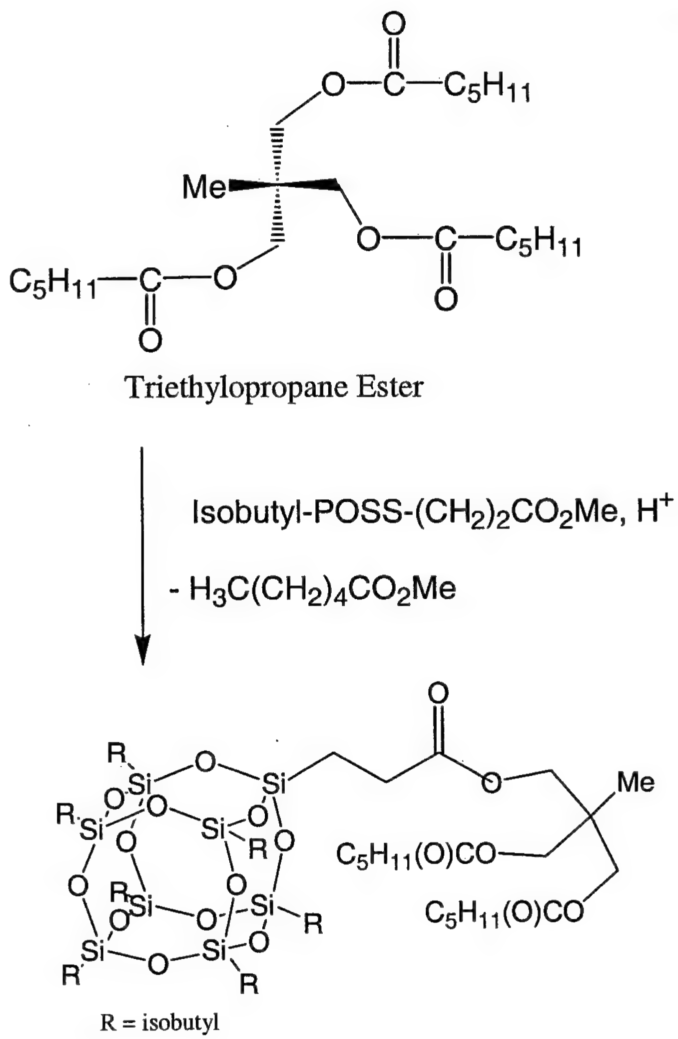
POSS Esters by Transesterification



- The Transesterification of POSS into the triester would result in a "larger" lubricant
- A transesterification was done with the cyclopentyl POSS derivative, but there was a very low conversion and the product could not be separated from the POSS starting material
- Is there another POSS we can try?

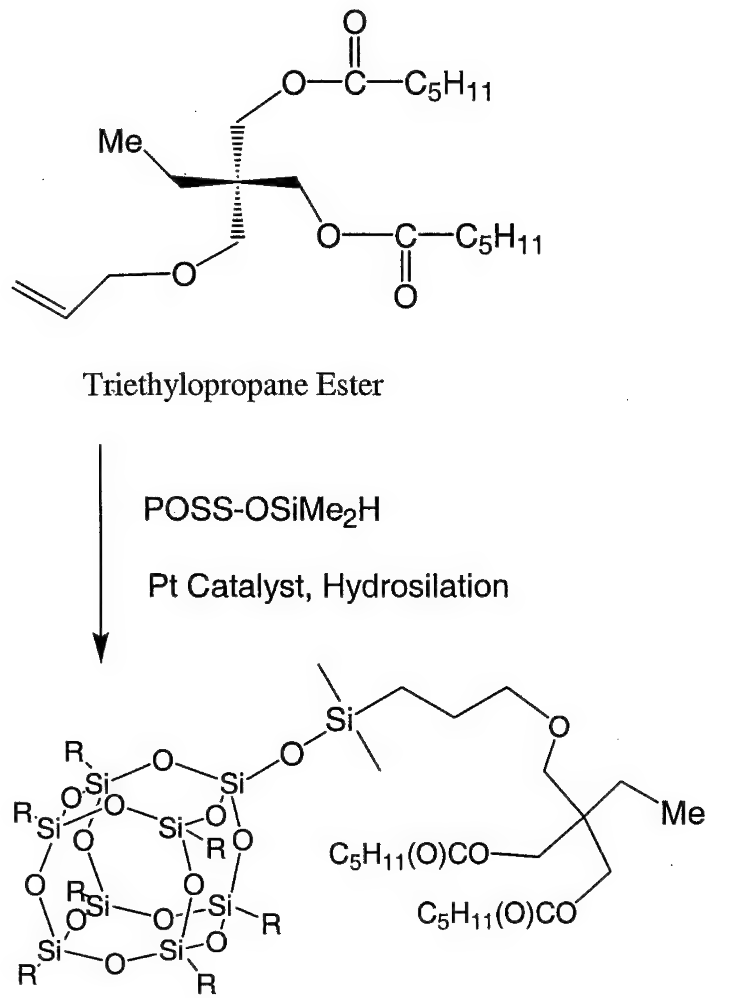
YES!

POSS Esters by Transesterification



- The Transesterification of the new very soluble and lower melting isobutyl POSS was attempted with our model base stock
- The conversion for this reaction was much higher than the previous reaction
- Attempts at isolating the product from the starting material proved to be unsuccessful
- Is there another pathway?

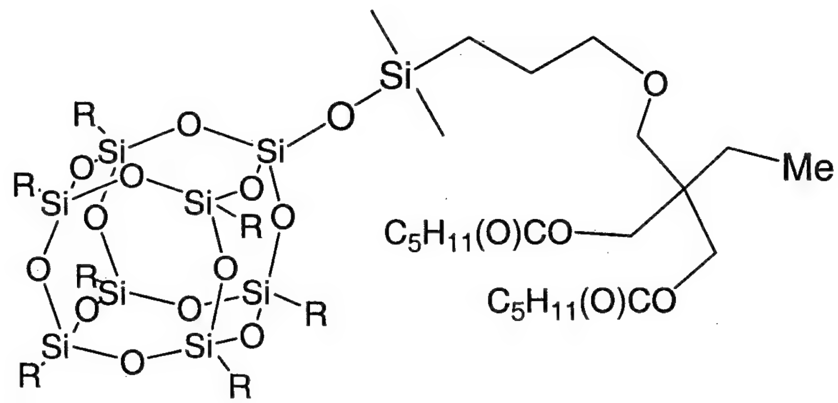
POSS Esters by Hydrosilation



R = cyclopentyl

- After several attempts to make a POSS ester (discussed previously), the hydrosilation of a POSS hydride with TMP allyl ether dihexanoate does give a POSS diester
- 3 grams made
- Solid (as expected)
- Solubility in ester base stock: low (< 2%)
- Thermal stability can still be tested

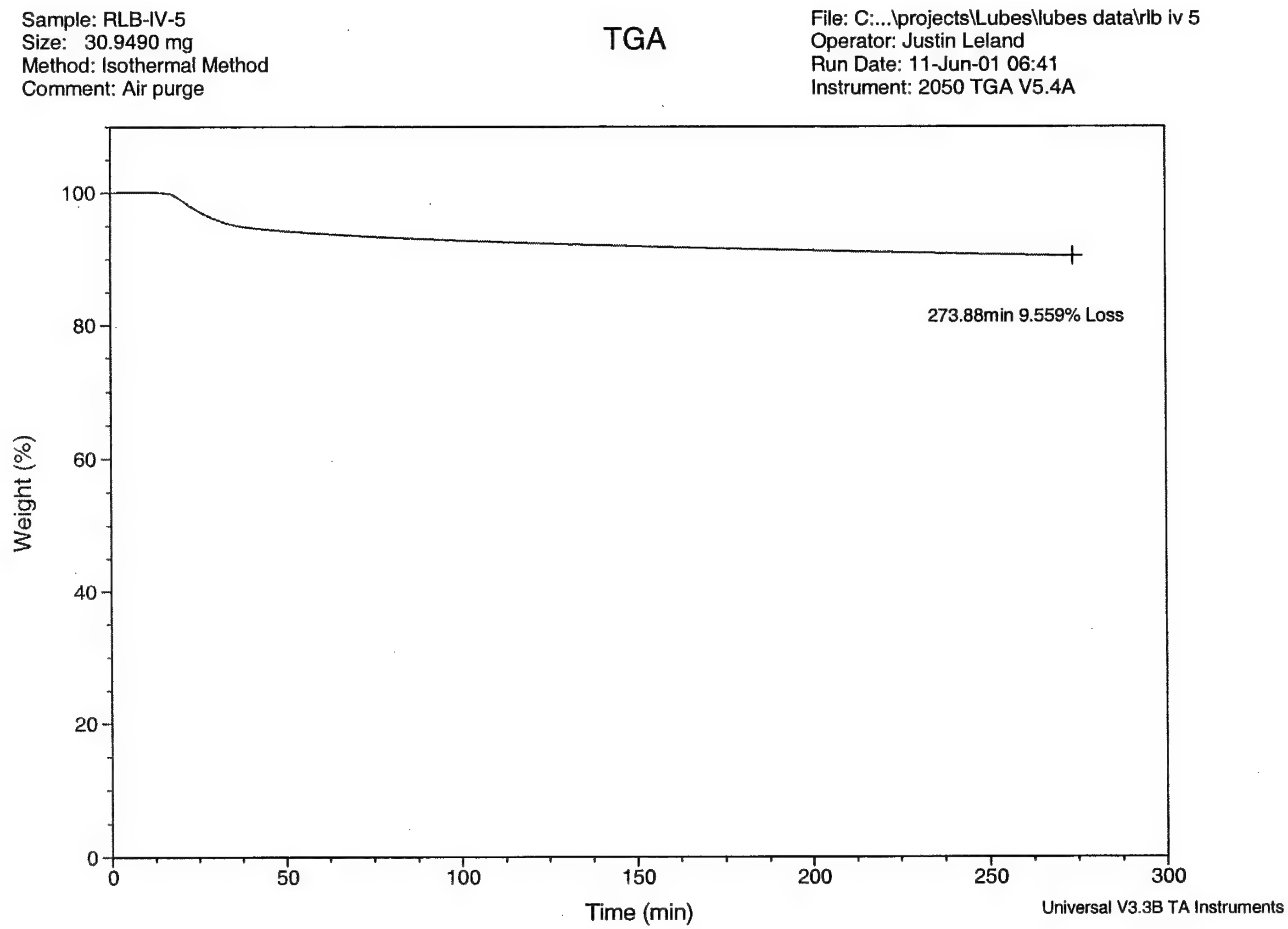
POSS Diester Formulation



White solid

- **An initial TGA in air showed a 10% loss after 274 minutes at 200 °C.**
- **A standard aminic AO package was added to the POSS diester and a 10% weight loss was observed after 448 min at 200 °C.**

TGA Data For POSS Diester w/o AO

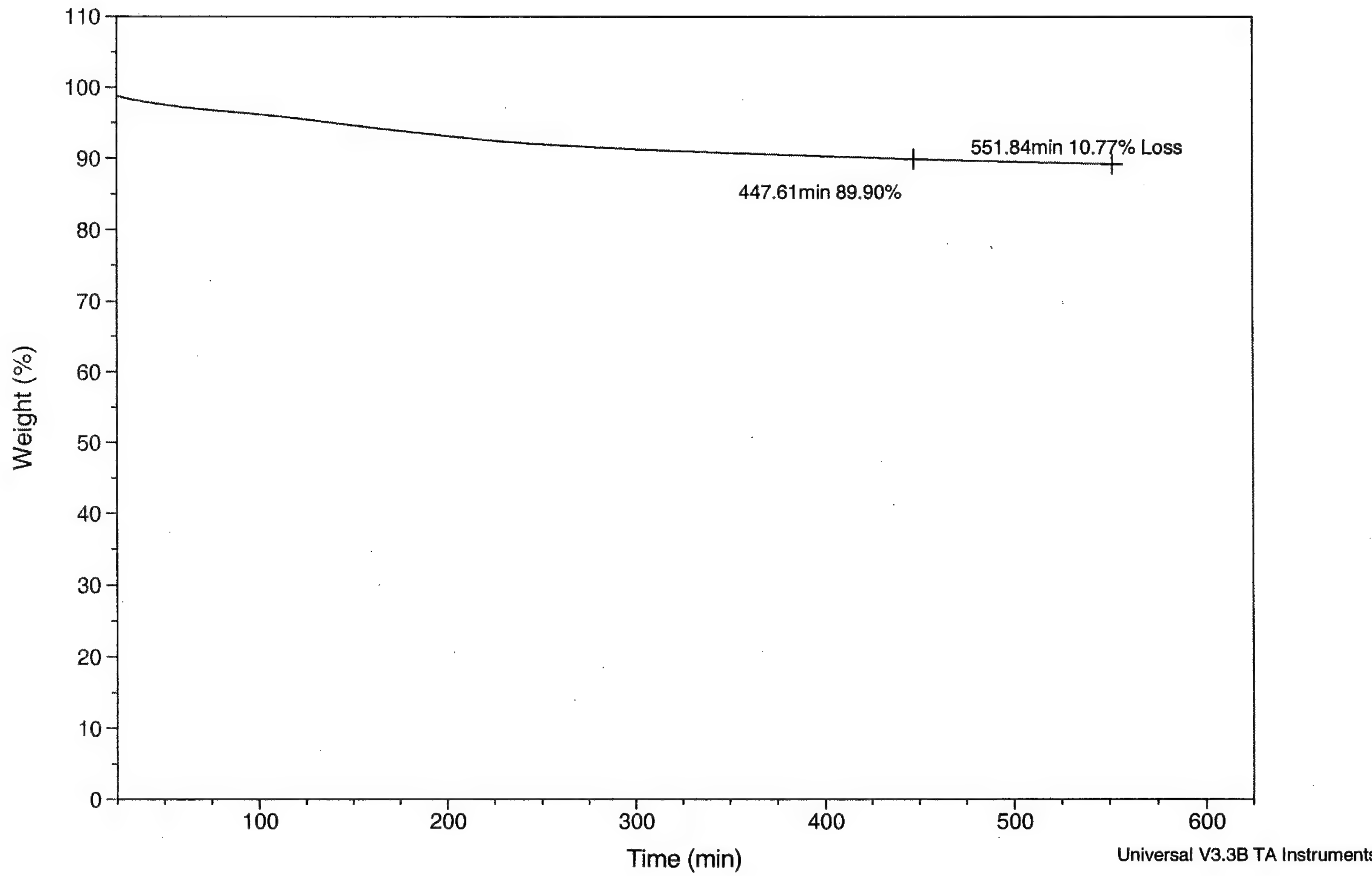


TGA Data For POSS Diester W/AO

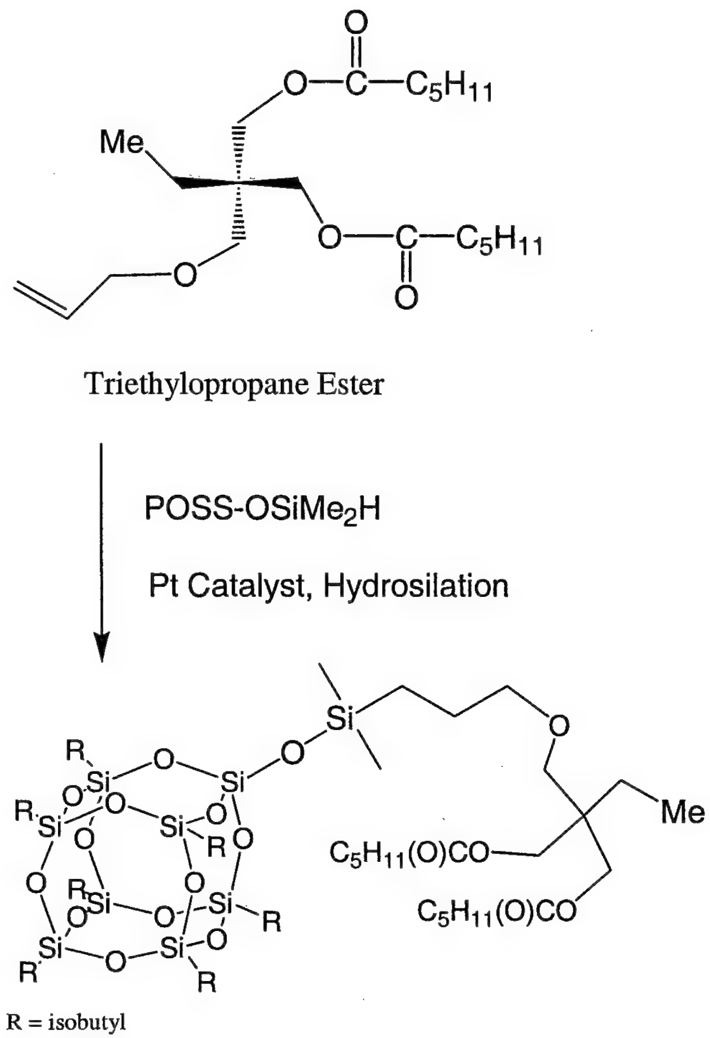
Sample: RLB-IV-5 w/AO
Size: 34.2630 mg
Method: Isothermal Method
Comment: Air purge

TGA

File: C:\TA\Data\Justin\TGA\RUSTY.001
Operator: Justin Leland
Run Date: 11-Jun-01 13:39
Instrument: 2050 TGA V5.4A

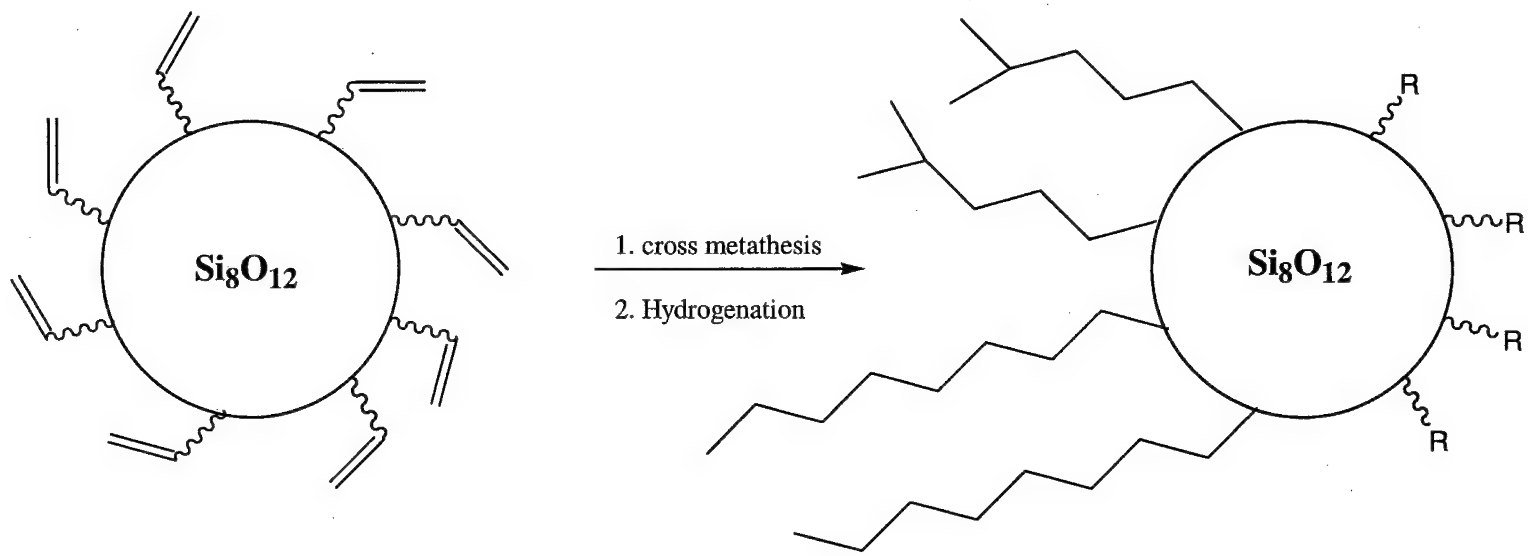


More Soluble POSS Diester



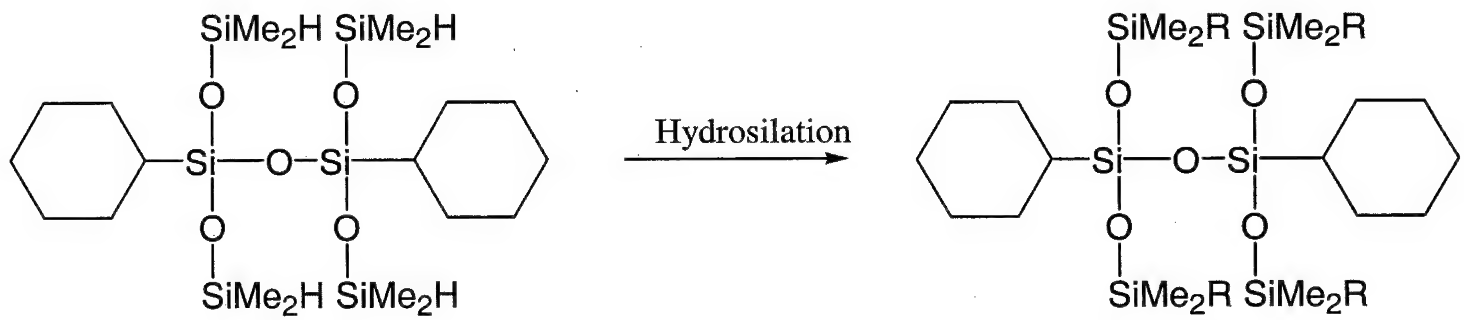
- A new POSS feedstock has come online with Hybrid Plastics: a POSS cage with isobutyl groups
- 3 grams made to prove concept
- Research problems (separation of unreacted TMP diester from POSS diester was not trivial due to similar solubilities) were overcome: vacuum distillation!
- Waxy Solid at room temperature
- Solubility in Grade 4 ester base stock: High, can be used in additive testing
- Further Physical testing will be done shortly

POSS Lubricants: T8 Class



- Stable above 200 °C (TGA)
- Oil at Room Temperature
- Through Cross Metathesis, Vinyl Groups allow adjustability of side groups

POSS Lubricants: CyT_2 Class



R= Decyl, Dodecyl, Tetradecyl , all liquids at RT

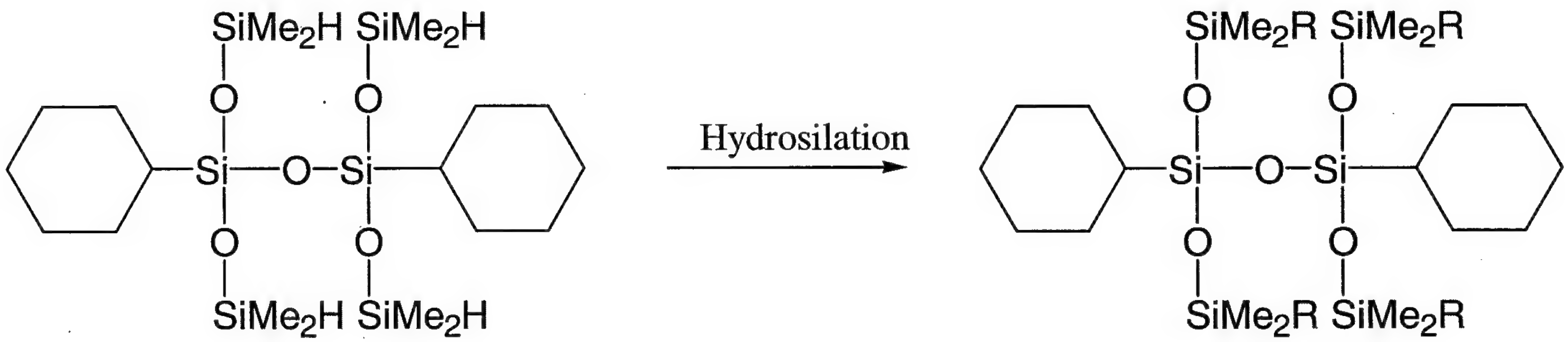
R=Octyl , flows at low Temp (-60 ºC), evaporates at 200 °C

R=Decyl the viscosity at –40 °C is 4000 cP !!

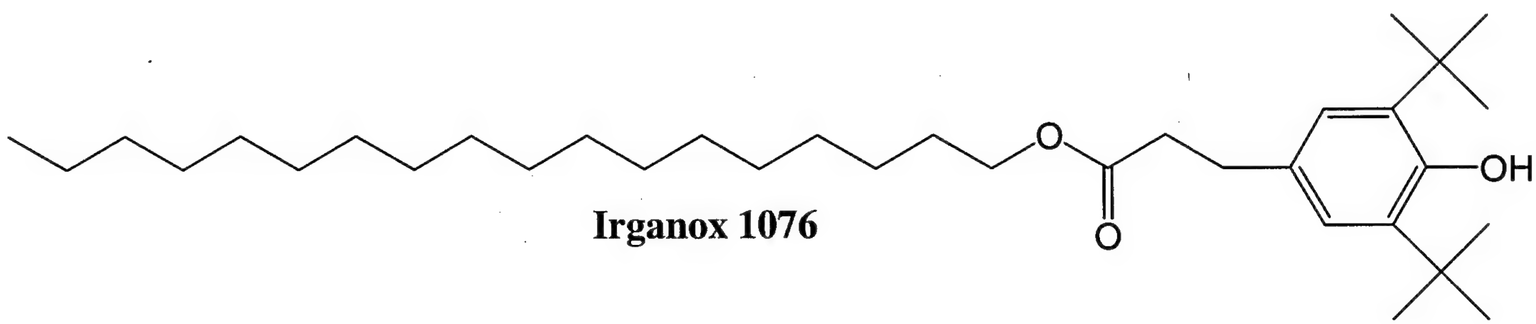
R=Dodecyl, the freezing point is -12 °C

Stable at 200 °C with A/O present (TGA)

T_2Tetradecyl System



R= Decyl



Irganox 1076

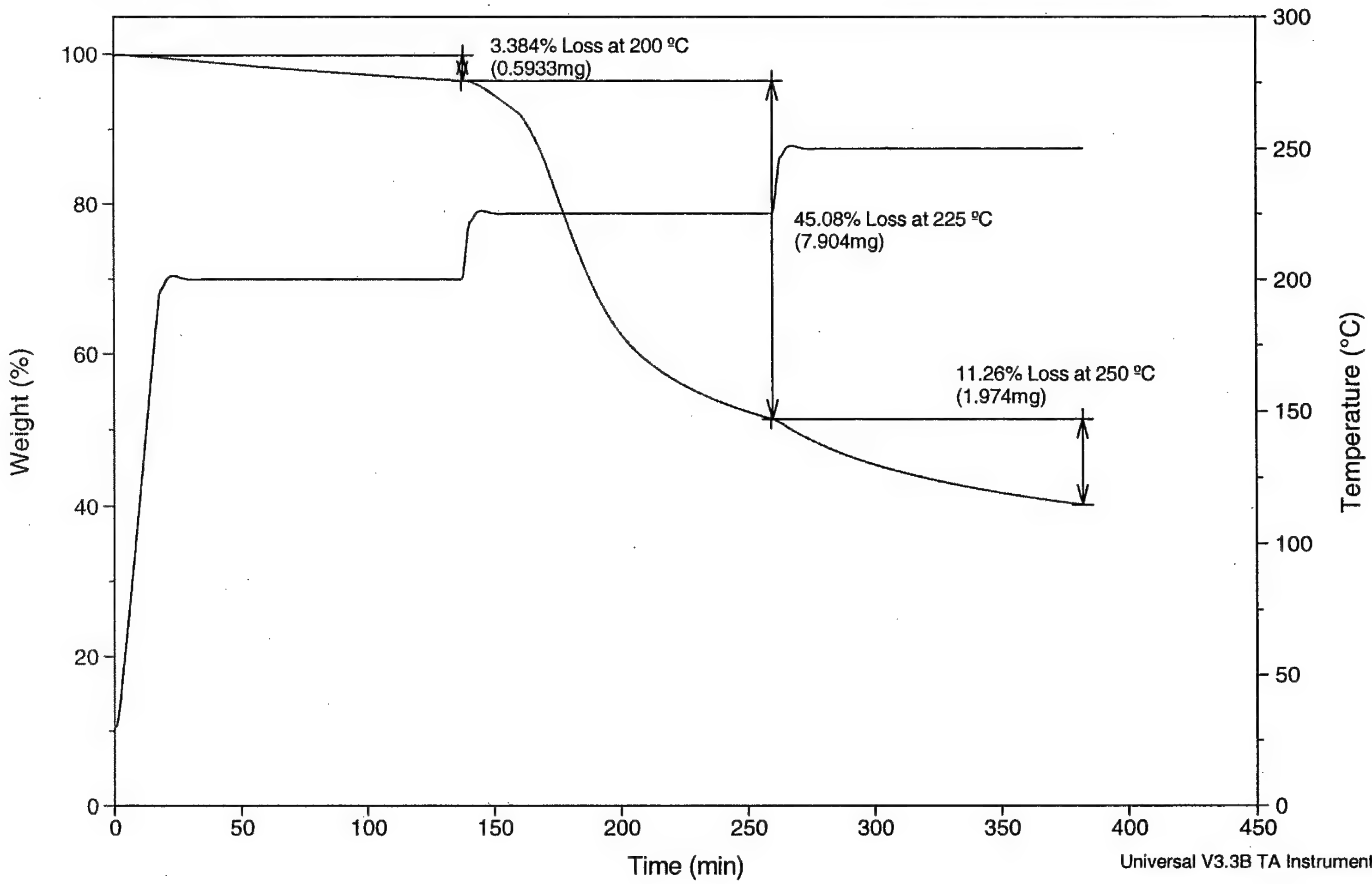
- **Aminic antioxidants reduce performance**
- **Irganox 1076 soluble to 4% level**
- **Higher temperature study performed:**

T_2 Tetradecyl System TGA

Sample: JTLI126 with 5% I-1076
Size: 17.5340 mg
Method: rampedisothermal
Comment: Air purge

TGA

File: C:\TA\Data\Justin\TGA\5WT250
Operator: Justin Leland
Run Date: 7-May-01 07:05
Instrument: 2050 TGA V5.4A



Universal V3.3B TA Instruments

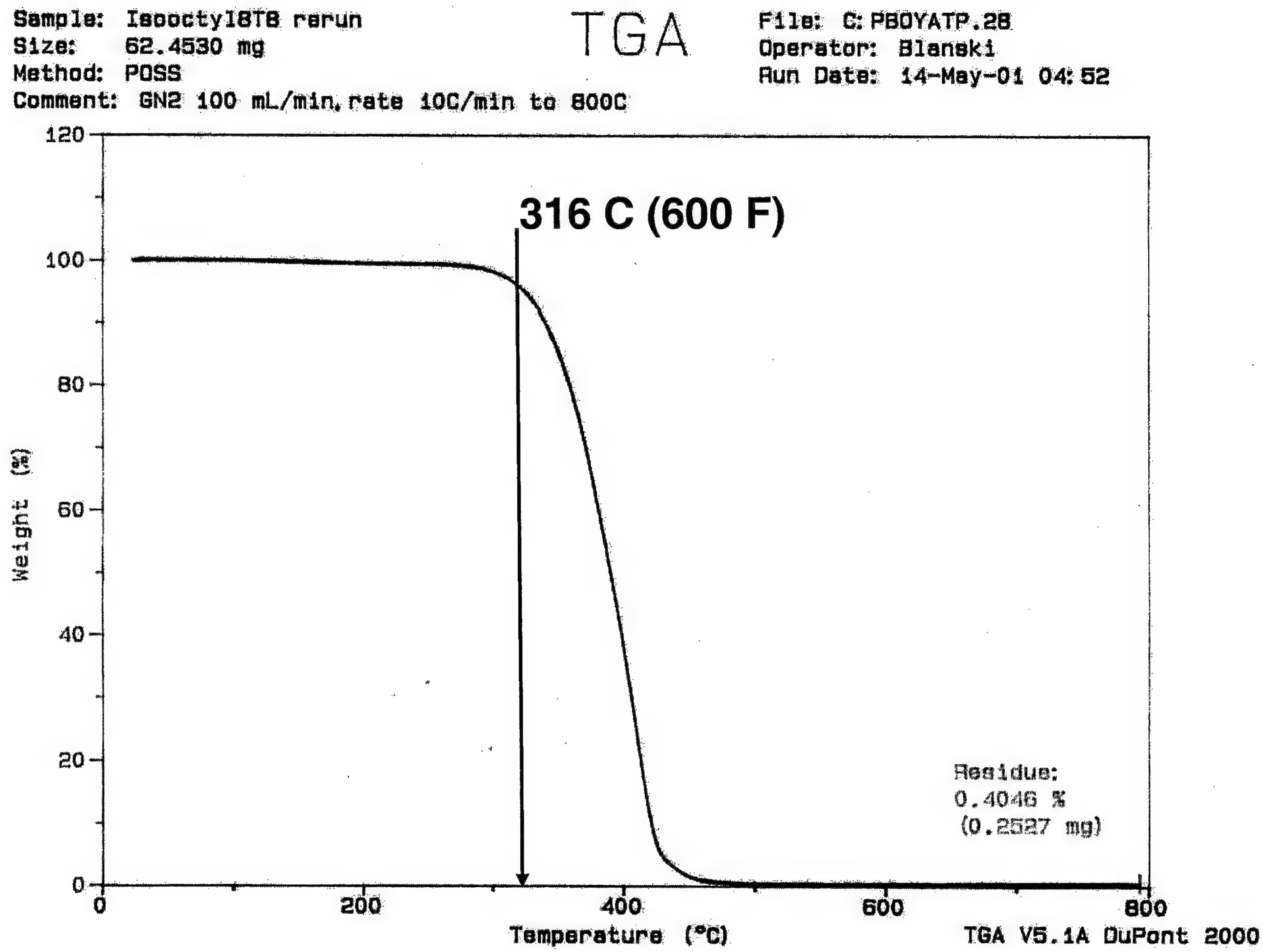
T_2Tetradecyl System

- While the T_2Tetradecyl system met the specifications for the state of the art (pourable at -40 ºF and stable at 400 ºF, the TGA data show that there are problems at higher temperatures: not an encouraging result
- To improve these results, a more efficient and compatible antioxidant may work → Further study
- While we do these studies, let's look into other systems.

New POSS Compounds

- In conjunction with Hybrid Plastics a series of compounds was analyzed by several methods. One of these compounds was $Isooctyl_nT_n$, a commercially available product which is an oil at room temperature (13100 cP at 20 ºC)
- One of these methods was Thermogravimetric analysis with an FTIR analysis of the effluent (TGA-FTIR)
- The POSS monomers usually did one of two things in the TGA-FTIR experiment: decomposed above 300 ºC or volatilized around 250 ºC. One sample however didn't volatilize until over 300 ºC (570 ºF): $Isooctyl_nT_n$
- What about using $Isooctyl_nT_n$ as a lubricant?

Isooctyl$_n$T$_n$ as a Lubricant

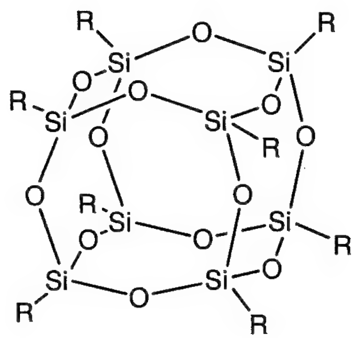


$Isooctyl_nT_n$ as a Lubricant

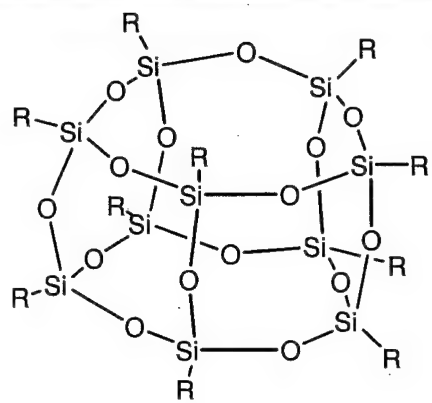
- Advantages of $Isooctyl_nT_n$ as a lubricant: potential high temperature stability and relatively low cost.
- Technical Challenges for using $Isooctyl_nT_n$ as a lubricant:
- Current supply of $Isooctyl_nT_n$ contains a small amount of resin which should be removed because of reactivity and viscosity concerns
- No known method available separate a POSS oil monomer from oily resin: the usual method of selective crystallization is impossible
- Low Temperature pourability issues

- Goals:
- Develop method to separate POSS oil monomer from resin
- Characterize pure oil and test decomposition temperature

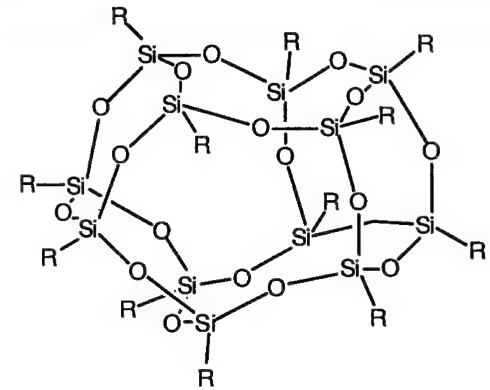
Isooctyl$_n$T$_n$ as a Lubricant



R = Isooctyl
minor component



R = Isooctyl
major component

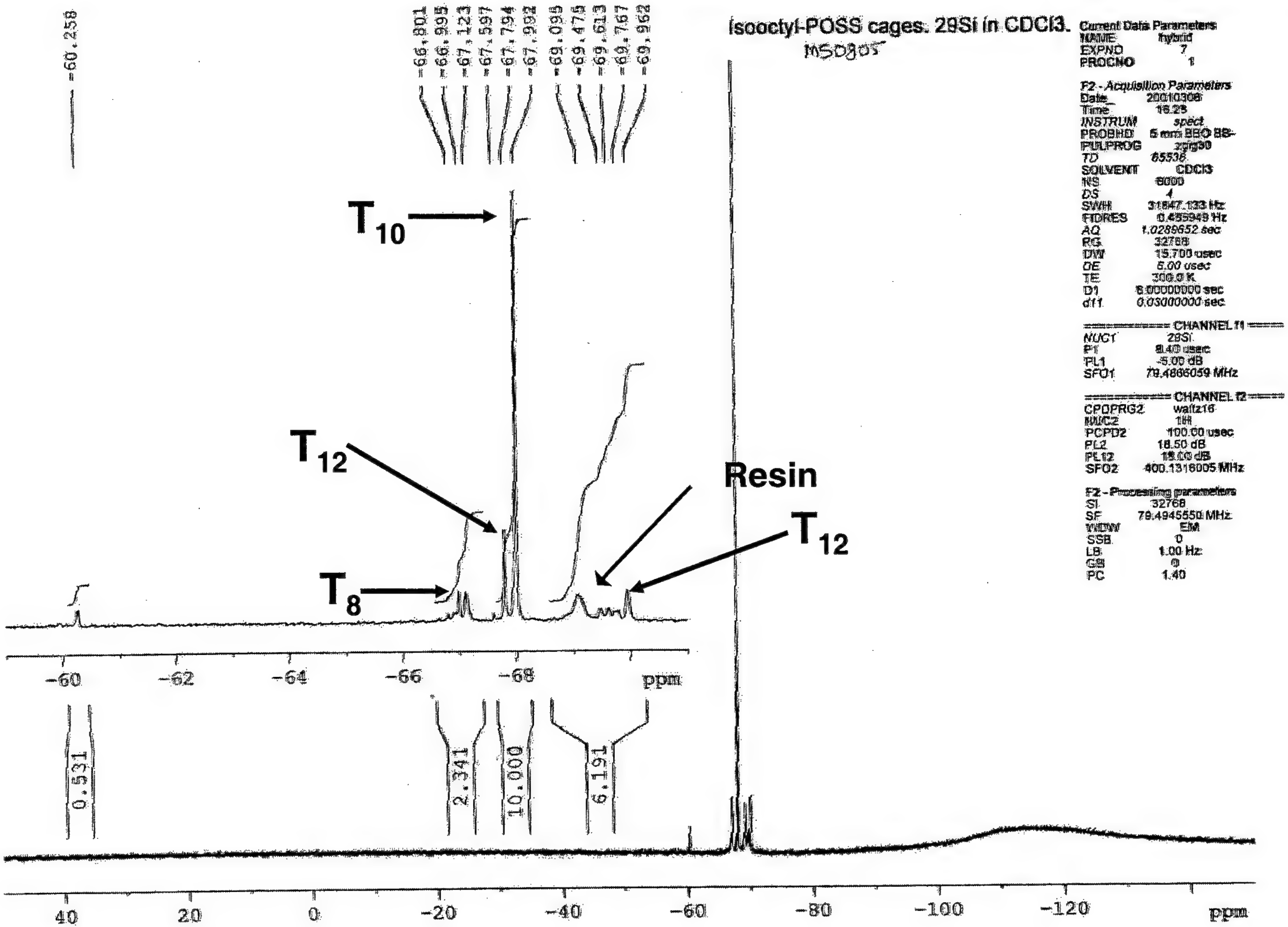


R = Isooctyl
minor component

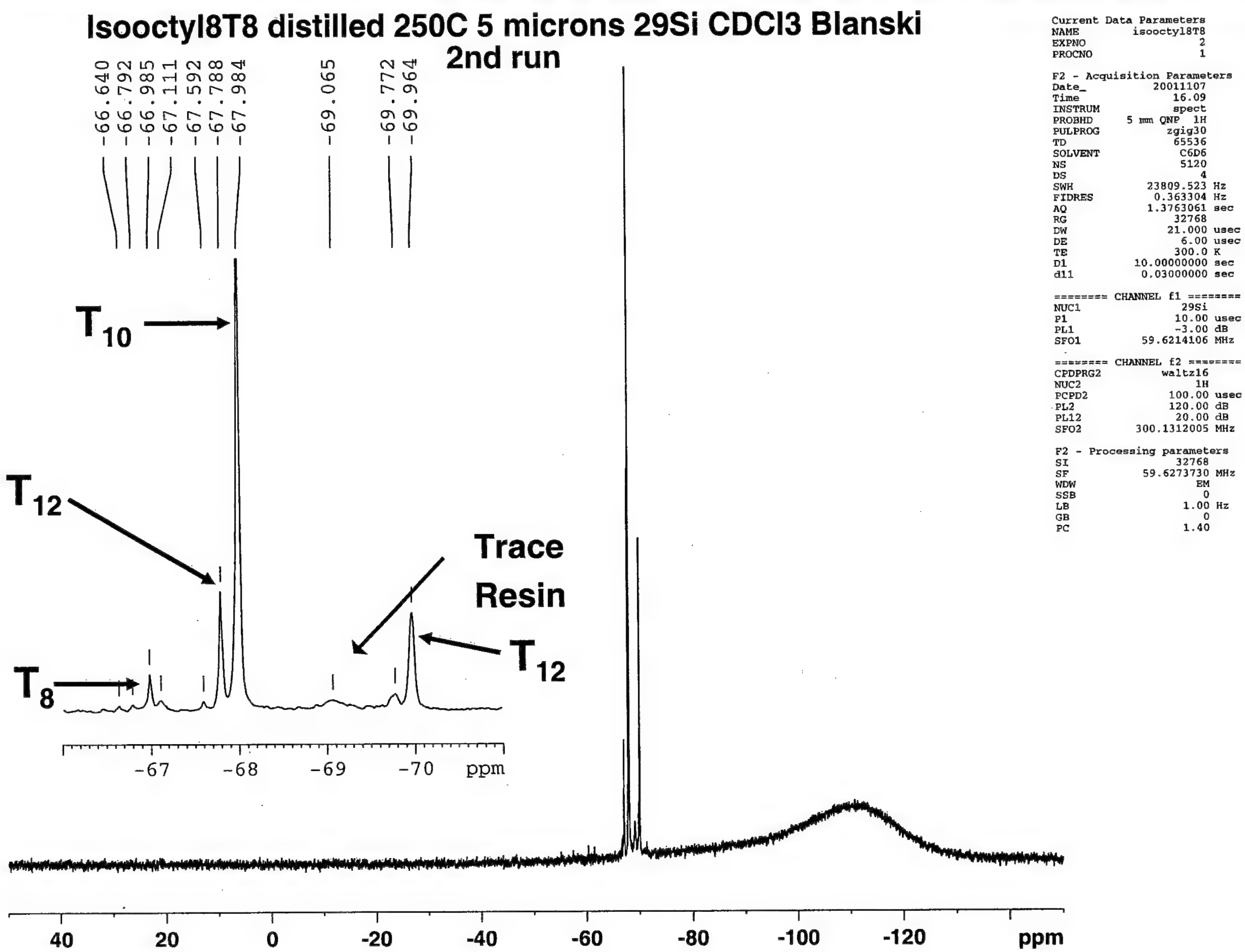
Since Isooctyl$_n$T$_n$ volatilizes without decomposing (TGA-FTIR confirms this) what about distillation?

Since distillation at 300 ºC is difficult, a vacuum distillation with a Kugelrohr (short path distillation under High Vacuum) was attempted

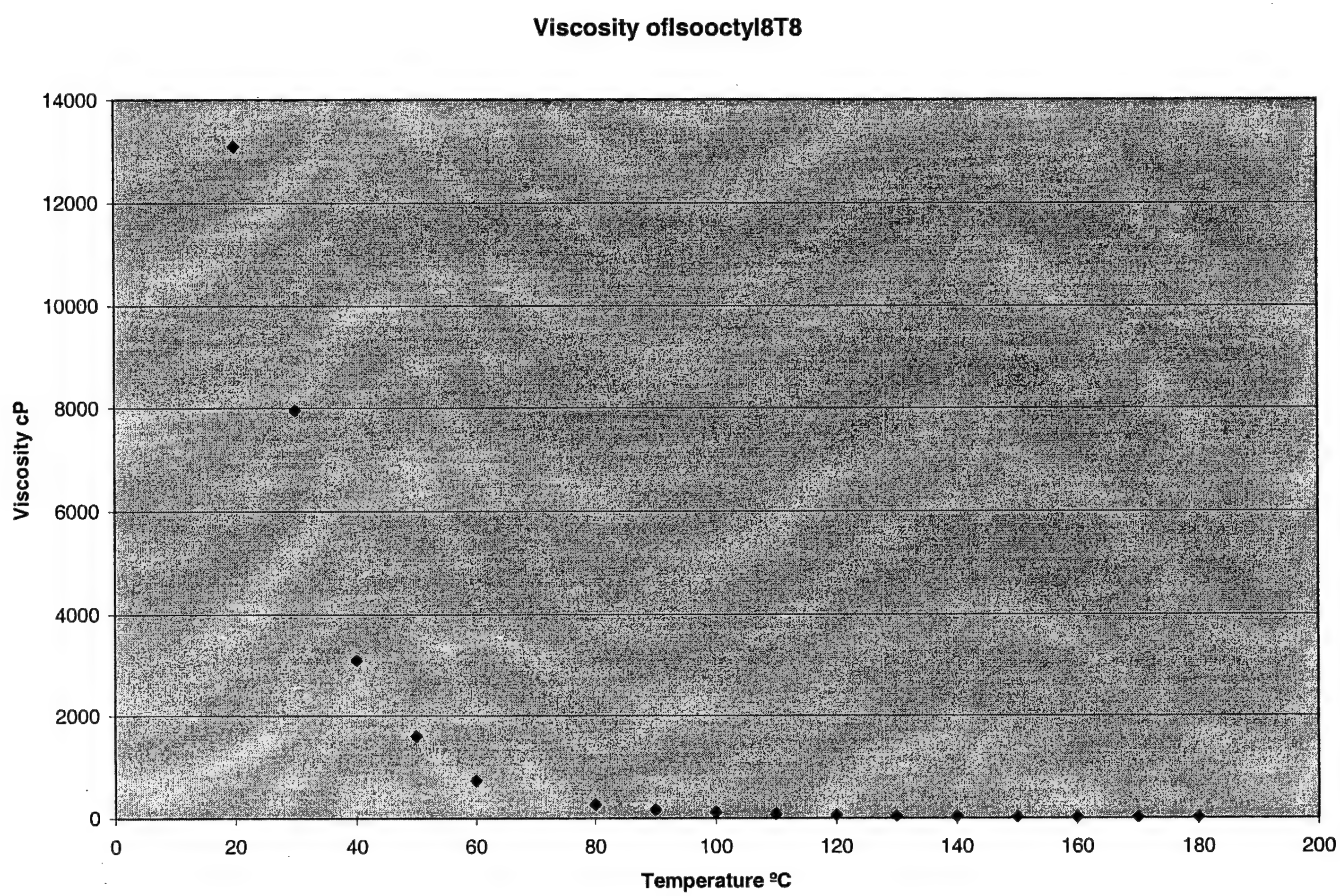
Isooctyl$_n$T$_n$ Before Distillation



$Isooctyl_nT_n$ After Distillation



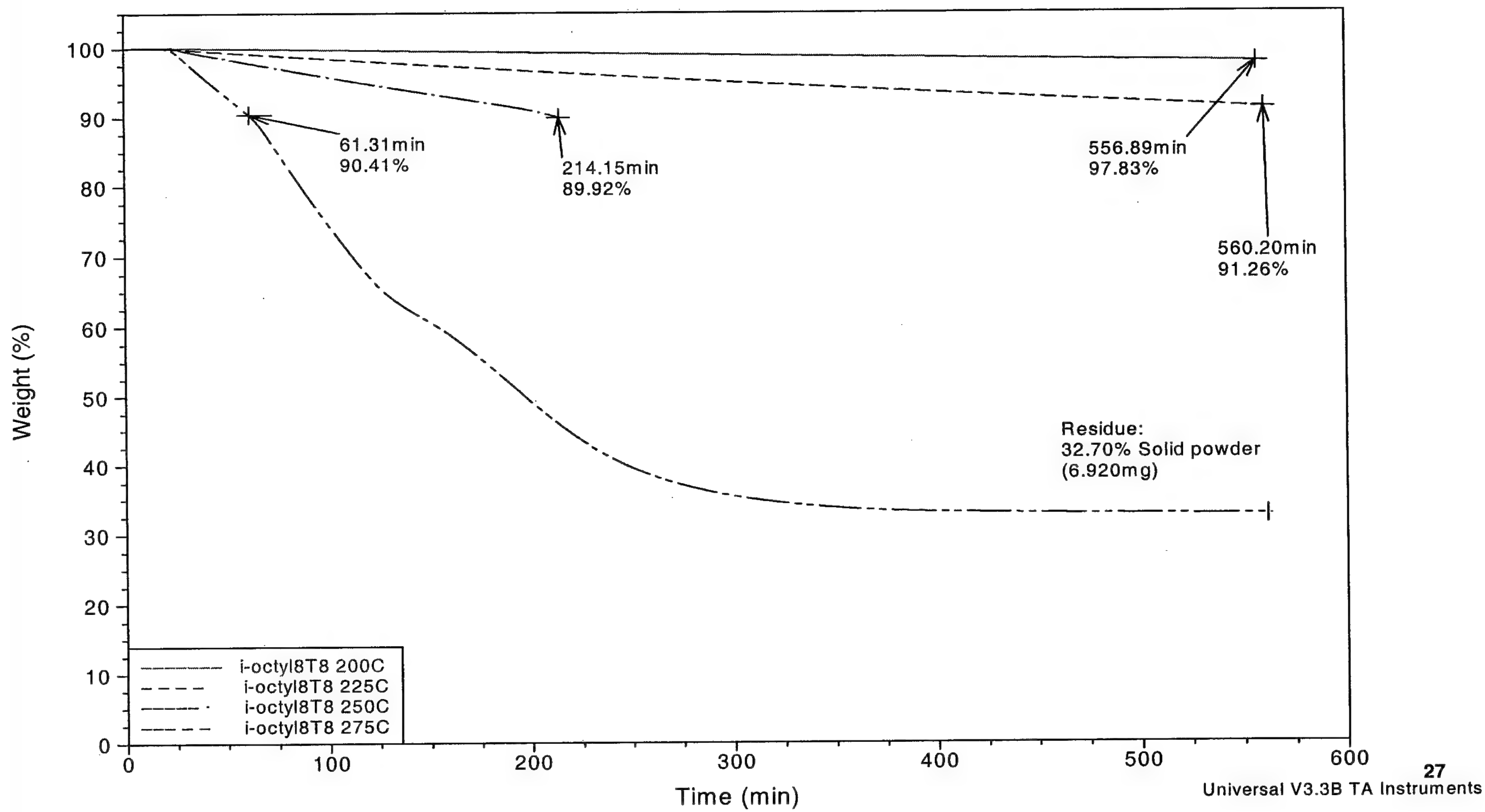
Viscosity of Distilled Isooctyl$_n$T$_n$



Temp °C	Vis cP
20	13100
30	7950
40	3100
50	1600
60	725
80	260
90	166
100	112.6
110	79
120	57
130	44
140	32
150	25
160	20.4
170	16.3
180	13.8

TGA of $\text{Isooctyl}_n\text{T}_n$ w/AO

i-octyl 8T8. All samples contain 5 wt% I-1076.



TGA of $Isooctyl_nT_n$ w/different AOs

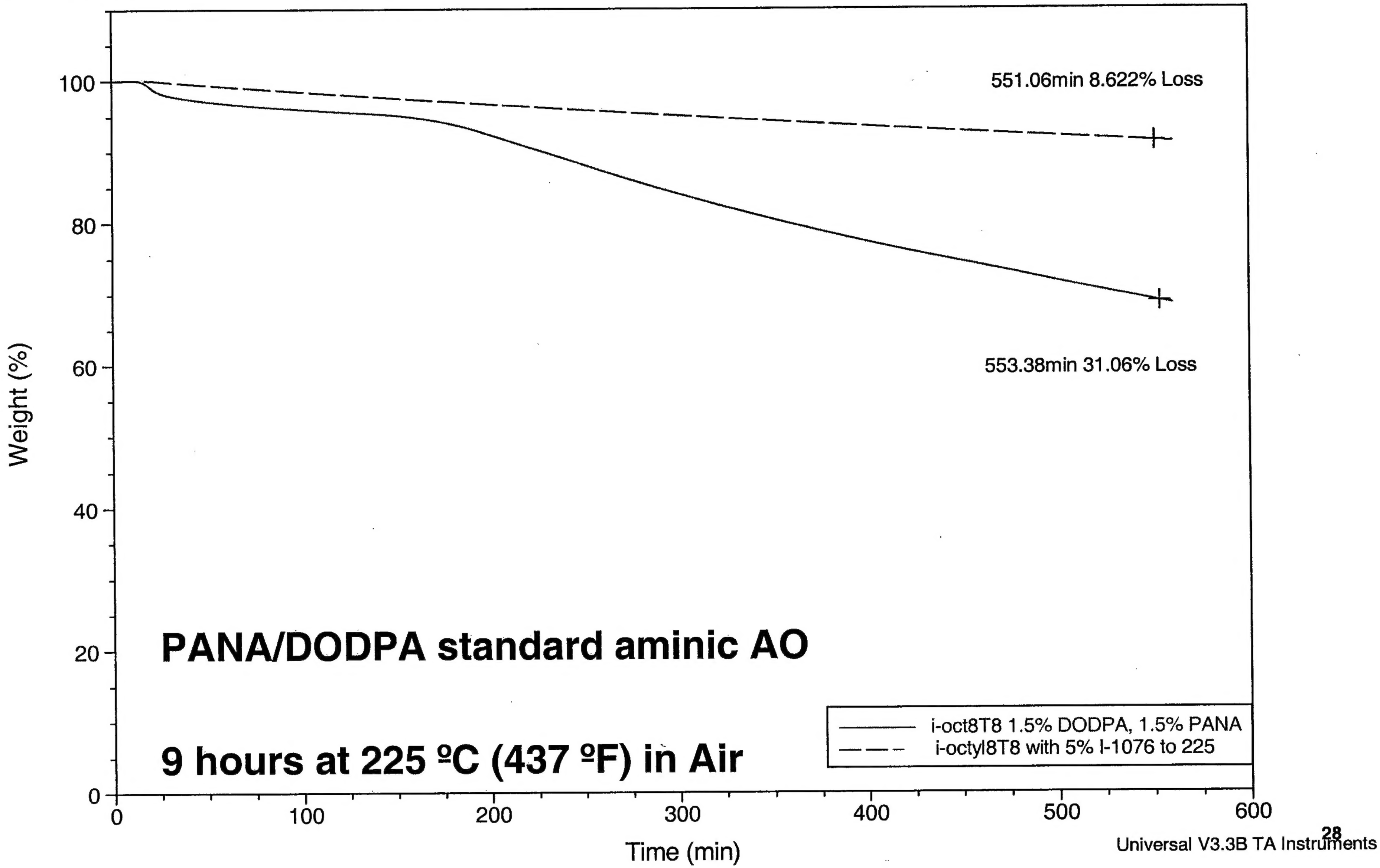


Table of TGA Data For POSS Samples

Material	TGA temp	TGA temp	Time to 10% mass loss	% lost after 9 hrs	residue
POSS Diester	200 °C	392 °F	4.6 hr	Stopped @ 4.6hrs	Solid
POSS Diester w/ AO	200 °C	392°F	7.5 hr	11	Solid
Isooctyl$_8$T$_8$ with 5% I-1076	200 °C	392 °F	--	2.2	Oil
Isooctyl$_8$T$_8$ with 5% I-1076	225 °C	437 °F	--	9.0	Oil
Isooctyl$_8$T$_8$ with 5% I-1076	250 °C	482 °F	3.5 hrs	Stopped @ 3.5hrs	Oil
Isooctyl$_8$T$_8$ with 5% I-1076	275 °C	527 °F	1hr	70	Grit

Future Work

- Perform Testing on POSS diester and make a POSS diester which is an oil at room temperature
- Finish testing for T2 work to determine high temperature stability of this system
- Perform further testing on $Isooctyl_nT_n$ (both purified and unpurified)

Conclusions: POSS Lubes

-POSS Esters can be made by the Hydrosilation of POSS hydride and an allyl ether TMP diester

-POSS oils can be made to flow at low temperature and are stable at higher temperature (Both theT_2s and the larger T_8s)

- The discovery of IsooctylnTn and its high temperature stability (> 225 C) opens the door to high temperature applications